Reduced graphene oxide aerogels with adjustable porosity as mesostructured support for catalysts and electrocatalysts.

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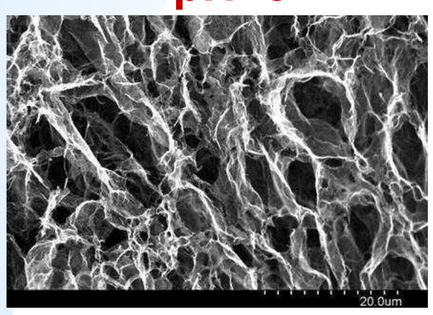
Motivation

- The translation of the properties of graphene to 3-D structures is of a great interest for catalysis, electrocatalysis and energy storage.
- However, graphene is prone to stacking to by van der Waals forces losing its properties and surface area
- Graphene aerogels can circumvent the stacking problem keeping interesting properties such as high surface area, open macroporosity for the diffusion of bulky molecules, flexibility, mechanical resistance, thermal and electrical conductivity.
- Here it is shown the possibility to control the porosity, mesostructure and surface chemistry of reduced graphene oxide aerogels and examples are shown about its use as catalyst and electrocatalyst support.

pH of GO dispersion effect

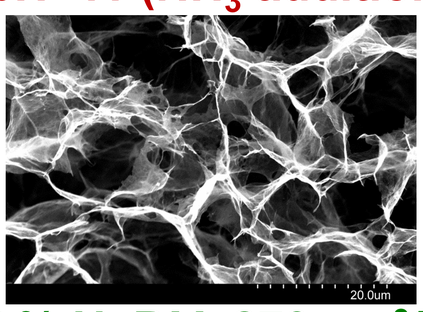
Hydrothermal reduction → **Freeze drying**

pH=3



0.5 % N, P.V.=128 cm^3/g

pH=11 (NH_3 addition)

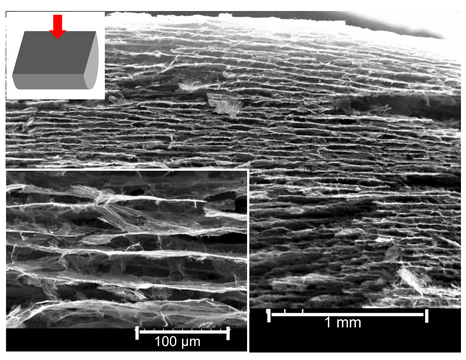


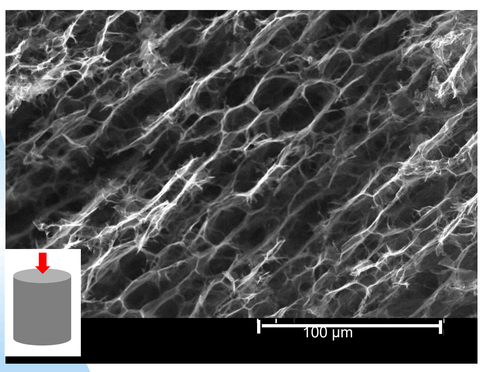
7 % N, P.V=273 cm^3/g

- Basic pH (NH_3 addition) leads to aerogels with larger pore volume, less stacking, twisted nanosheet morphology and a 7%Nitrogen content [1]

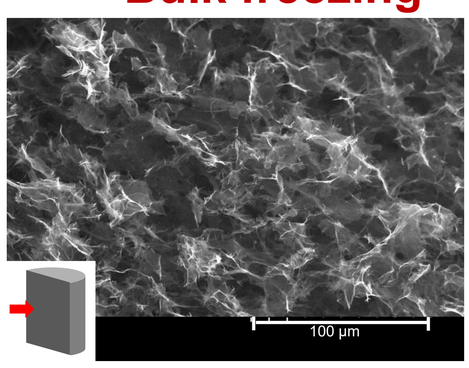
Freeze drying: unidirectional ice templating

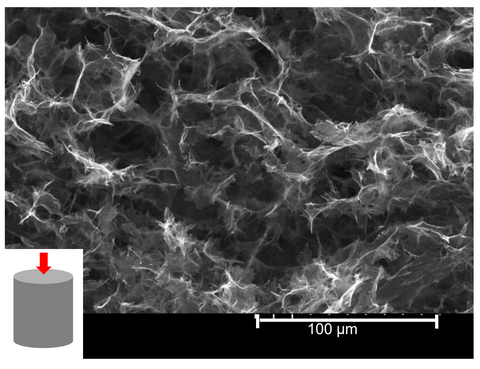
Unidirectional freezing





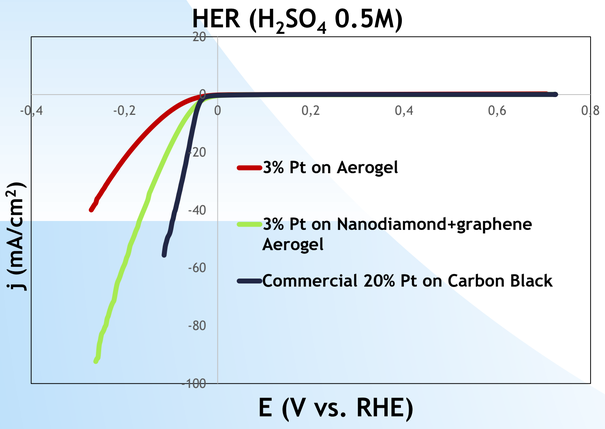
Bulk freezing

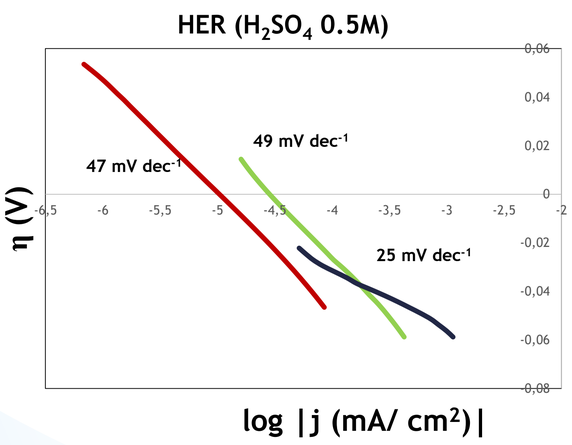




- Unidirectional freezing before freeze drying leads to aerogels with unidirectional pores favorable for nanofluidics in structured catalyst[2].

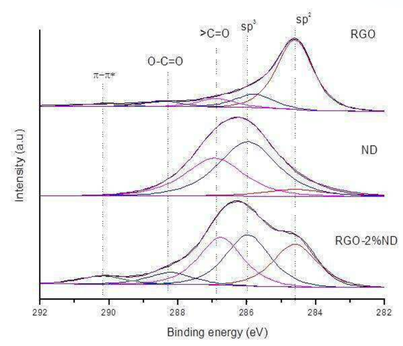
rGO aerogels as electrocatalyst support

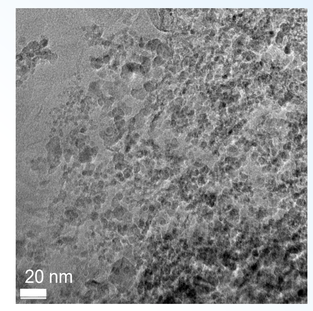


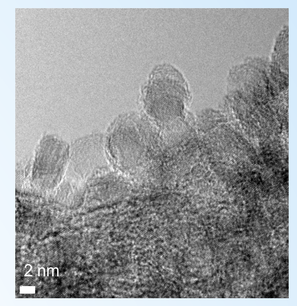


- Different mechanism of Pt catalyst supported on graphene and on carbon black

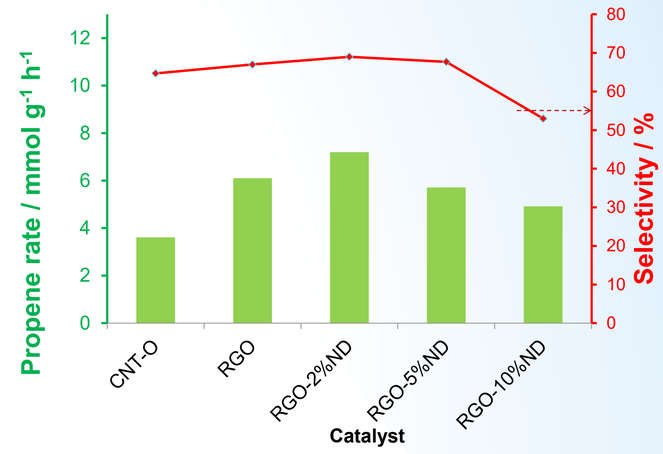
rGO aerogels as nanodiamond support for propane dehydrogenation



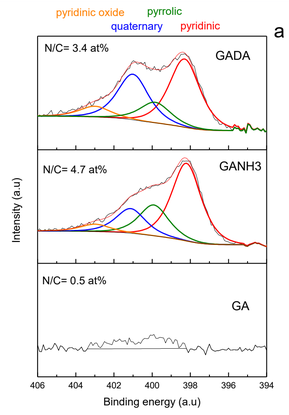


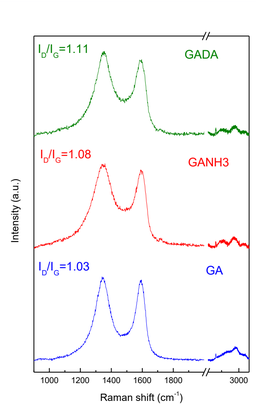


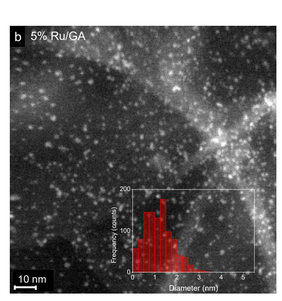
- nanodiamonds are well dispersed on graphene aerogels up to a 2% loading [3].
- the sp^3/sp^2 ratio measured by XPS is higher for the ND graphene aerogel hybrid
- the hybrid with ND exhibits higher activity in propane dehydrogenation

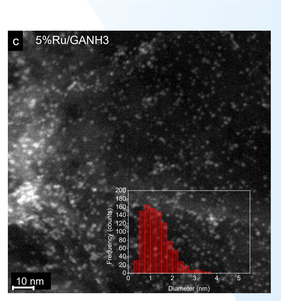


Ru on polydopamine coated rGO aerogels



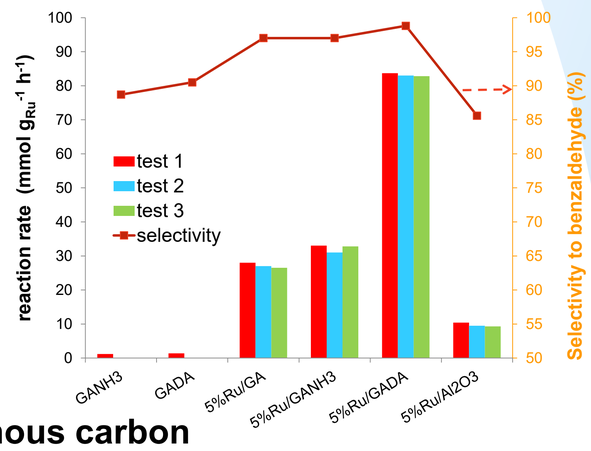






rGO aerogel supports:

- GA: aerogel without NH_3. N=0.5%
- GADA: aerogel coated with polydopamine-derived carbon. N=3.4%
- GANH3: aerogel with NH_3. N=4.7 %



- XPS:GADA 30% quaternary N, while GANH3 only 15%
- Raman: GADA contains more amorphous carbon
- TEM: Ru nanoparticles (1 nm average size) well dispersed on graphene nanosheets
- GADA support provides more activity and selectivity in benzyl alcohol oxidation

CONCLUSIONS

- The addition of NH_3 affects the graphene morphology , reduction degree, morfology of rGO nanosheets and introduces a 7 % on N.
- rGO aerogels of unidirectional pores have been synthetised by unidirectional freezing.
- rGO aerogels have been used as support of nanodiamonds and noble metal (Ru, Ni)
- Nanodiamond supported graphene aerogels have been used as metal free catalyst in propane dehydrogenation
- Highly dispersed noble metals have been tested in benzyl alcohol selective oxidation and as electrocatalytst in HER

References:

[1] E. Garcia-Bordeje, S. Victor-Roman, O. Sanahuja-Parejo, A.M. Benito, W.K. Maser, *Nanoscale*, 10 (2018) 3526-3539.

[2] V. Rodríguez-Mata, J.M. González-Domínguez, A.M. Benito, W.K. Maser, E. García-Bordejé, *ACS Applied Nano Materials*, 2 (2019) 1210-1222.

[3] L. Roldan, A.M. Benito, E. Garcia-Bordeje, *Journal of Materials Chemistry A*, 3 (2015) 24379-24388.

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